NASA TT F-11, 709

SUPPLEMENT TO OUR COMMUNICATION ON FORMALDEHYDE AND FORMATE FORMATION

H. Euler and A. Euler

Translation of "Nachtrag zu unserer mittheilung über formaldehyd und formiatbildung."
Berichte der Deutschen Chemischen Gesellschaft, Berlin
Vol. 39, pp. 36-51, 1906.

Dent. Ges. Chem.

GPO PRICE $ _____

CFSTI PRICE(S) $ _____

Hard copy (HC) 3.00

Microfiche (MF) .65

ff 653 July 65

N68-30603

(ACCESSION NUMBER) (THRU)

13 1

(PAGES) (CODE)

✓ 06

(NASA CR OR TMX OR AD NUMBER) (CATEGORY)

FACILITY FORM 602

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 JULY 1968

6. SUPPLEMENT TO OUR COMMUNICATION ON FORMALDEHYDE AND FORMATE FORMATION

H. Euler and A. Euler
Stockholm Technical Institute

ABSTRACT: Three separate papers are presented, dealing respectively with the condition under which formaldehyde is converted to formate by bases, the formation of sugar from formaldehyde, and the formation of i-arabinoketose from formaldehyde.

In the course of our investigation of carbon assimilation and sugar formation [1], it appeared to us to be desirable to establish the conditions under which formaldehyde is converted to formate by bases. The study of this reaction suggested that formates are generated via the salts of formaldehyde as intermediates. This conclusion was proven by direct measurements of salt formation or of the hydrolysis of the sodium salt of formaldehyde (sodium formolate). [The terminology here and in some later passages is obsolete but is translated as literally as possible to reflect the author's intent.—Translator]. /36* /37

According to the experiments previously communicated, the strength (dissociation constant) of formaldehyde as an acid is found to be $1 \cdot 10^{-14}$.

This confirms our conclusion which had been based on the course of formate formation.

Mr. Auerbach [2], believes he is obligated to draw our attention to the deficiencies in our investigation, and indicates that they "indeed affect only the quantitative results of the Eulers' investigations, while the results are qualitatively confirmed."

The following data show the extent to which this assertion is justified.

As the course of our work, and especially the formulation of our results clearly indicate, it occurred to us, after we had confirmed the formation of formaldehyde salts, to determine the order of magnitude of the dissociation constants of the formaldehyde salts. Therefore we attached no importance to the preparation of completely methyl alcohol-free solutions of formaldehyde; for the methyl alcohol content of our solutions could have no significant effect on our results, as the analysis of our solutions by the Legler method showed. The latter method was chosen in view of the rapidity with which it could be carried out. The method of preparation of pure methyl alcohol-free formaldehyde solutions has, of course, long been known through the investigations of Tollens, which we have also mentioned. His investigations demonstrate how pure formaldehyde solutions can

*Numbers in the margin indicate pagination in the foreign text.

be prepared by dissolving trioxymethylene, which in turn is made from ordinary formaldehyde ("formol") solutions. We have also used the pure solutions in our saponification experiments.

Since our measurements were carried out (summer of 1904), W. Fresenius and L. Grünhut [3] have critically examined the analytical methods for formaldehyde and have shown the accuracy of the Romijn iodometric method. The solutions used in the following experiments were analyzed by the Romijn method. The freezing point depressions of the solution, and the method of chemical analysis, gave concentration values which agreed within one percent. Calculations were performed using the averages of the two determinations.

/38

Mixture of equal volumes	Freezing point depression
I	
0.65 *n*. $CH_2O + H_2O$	$J_1 = 0.60$
0.66-*n*. $NaOH + H_2O$	$J_2 = 1.17$
	$J_1 + J_2 = 1.77$
0.65 *n*. $CH_2O + 0.66$-*n*. NaOH .	$J_3 = 1.40$
	$J_1 + J_2 - J_3 = 0.37$
II.	
1.00-*n*. $CH_2O + H_2O$	$J_1 = 0.93$
0.99-*n*. $NaOH + H_2O$	$J_2 = 1.71$
	$J_1 + J_2 = 2.64$
1.00-*n*. $CH_2O + 0.99$ *n*. NaOH .	$J_3 = 2.02$
	$J_1 + J_2 - J_3 = 0.62$
III.	
0.64-*n*. $CH_2O + H_2O$	$J_1 = 0.59$
1.00-*n*. $NaOH + H_2O$	$J_2 = 1.72$
	$J_1 + J_2 = 2.31$
0.64-*n*. $CH_2O + 1.00$ *n*. NaOH .	$J_3 = 1.87$
	$J_1 + J_2 - J_3 = 0.44$
IV.	
0.64-*n*. $CH_2O + H_2O$	$J_1 = 0.59$
0.50-*n*. $NaOH + H_2O$	$J_2 = 0.88$
	$J_1 + J_2 = 1.47$
0.64-*n*. $CH_2O + 0.50$-*n*. NaOH .	$J_3 = 1.17$
	$J_1 + J_2 - J_3 = 0.30$
V.	
0.50-*n*. $CH_2O + H_2O$	$J_1 = 0.47$
0.50-*n*. $NaOH + H_2O$	$J_2 = 0.47$
	$J_1 + J_2 = 1.34$
0.50-*n*. $CH_2O + 0.50$-*n*. NaOH .	$J_3 = 1.10$
	$J_1 + J_2 - J_3 = 0.25$

If the dissociation constant of formaldehyde is calculated from these experimental results* using the law of mass action, the value obtained is $1.4 \cdot 10^{-14}$ at 0°.

With regard to Mr. Auerbach's critique, we quote verbatim from our previous communication:

*As regards the molecular theoretical interpretation, let no one doubt that the two formulas depicted by Mr. Auerbach are essentially identical.

"The measurements reported can thus be summarized as follows: Formaldehyde is a weak acid, which forms salts with strong bases: a 1 normal solution of formaldehyde sodium salt contains approximately one-half of the salt as such, while half is dissociated into free base and free formaldehyde. In dilute solution, the formaldehyde salt may be treated as a binary electrolyte; the strength (dissociation constant) of formaldehyde as an acid amounts* to about $1 \cdot 10^{-14}$ at 0°." /39

Certainly, with enough time and effort, the experimental results could be given to an additional decimal place. If this task appears of sufficient interest to Mr. Auerbach, we would gladly grant it to him, along with the measurement of the migration rate of the complex methylene glycolide ion** which he also mentioned.

In pursuing our research plan, we have meanwhile investigated the condensation of formaldehyde and next report our results on the course and the end products of sugar formation.

7. ON THE FORMATION OF SUGAR FROM FORMALDEHYDE

H. Euler and A. Euler

Bases are known to react with formaldehyde, in part to produce formates and in part to cause condensation. We have previously investigated formate formation quantitatively [1]. The result of our measurements was that the dissolved bases possess a specific ability to produce formate, but that the ability of the various bases to condense formaldehyde, yielding sugar, does not have a direct relationship with the rate of formate formation.

We have further pursued the study with special consideration to the sugar condensation, and for this purpose we have investigated the general concentration conditions and limits for the formation of sugar. Except for isolated data***, the latter are still unknown. /40

*This may not be the place for the discussion of the application of the mass action law. An approximate calculation which is easily performed shows that the uncertainty caused by the assumptions made for the purposes of calculation is appreciably exceeded by that due to experimental error.

**We shall shortly return to our saponification experiments as well as to the amphoteric nature of formaldehyde and other aldehydes.

***O. Loew found that 3.5-4% formaldehyde, saturated with lime, is converted to sugar at ordinary temperature in the course of 5-6 days with simultaneous formation of formate, until the formaldehyde disappears. If the concentration of lime is too low, the condensation may fail to occur, while if the formaldehyde concentration is raised, too much of the aldehyde is converted to formate. Loew further showed that saturated lime water effects appreciable condensation in 1% formaldehyde solution at 100°, while barytes water (BaO) at the same dilution forms only a little sugar. Lobry de Bruyn and Alberda van Ekenstein then found that lead hydroxide freshly precipitated with lime is a condensing agent very much

After we had repeated Loew's experiments and had confirmed them, we extended them to an examination of the behavior of 4% (1.33 N) formaldehyde solution with lime at 100°. It was found that under these conditions, lime in quantities corresponding to 0.04 - 0.14 N solutions produces a detectable formation of sugar, to just as small an extent as does barytes — which is a poor condensation agent — in the same concentrations. Namely, under these conditions, lime and barytes converted the same amounts of formaldehyde which actually underwent reaction, exclusively into formate and methanol. In contrast, with an excess of lime in 4% formaldehyde solution, condensation occurred in a few minutes, corresponding to the behavior of this mixture in the cold.

Preliminary experiments,* at 100° or at the boiling points of the solutions, first gave the result that in 3.6% (1.2 N) formaldehyde solutions, no detectable amount of sugar is formed by boiling with:

Barytes in 0.007 - 0.06 N solution,
Lime in 0.007 - 2.12 N solution,
Sodium hydroxide in 0.025 N solution,
Zinc hydroxide, zinc hydroxide + 0.01 N sodium hydroxide,
Ferric hydroxide, ferric hydroxide + 2.02 N sodium hydroxide,
Soda and lithium carbonate in 0.1 N sodium hydroxide.

The soluble bases and carbonates are converted to formates. The zinc hydroxide is slowly dissolved by formaldehyde (about 1.5 g dissolved per liter of 1.2 N solution during the 14 hours of boiling); the solution contains zinc formate. The ferric hydroxide is attacked in at most trace amounts. /41

While a 0.9% (0.3 N) formaldehyde solution is more or less converted to sugar by 0.02 N lime or barytes (Loew), this solution with 0.01 N sodium hydroxide gives no detectable amount of sugar. In contrast, 0.01 N sodium hydroxide effects a significant degree of condensation in 0.15 N formaldehyde solution.

Thus it could be anticipated that at an appropriately chosen concentration of aldehyde, it would be possible to condense formaldehyde and form sugar with any soluble base; for poorly condensing bases, the concentration of formaldehyde solution in relation to the concentration of the bases need only be sufficiently low. The range of most suitable base concentrations is determined on the basis that on the one hand, too small amounts of bases to saturate the formic acid are consumed before sugar formation is achieved; on the other hand, large amounts of bases convert an undesirably large proportion of formaldehyde to formate.

In studying the condensation by means of sodium hydroxide, the use of soda [sodium carbonate—Trans.]** is especially worthy of recommendation, because

superior to those formerly known. Thus a 4% formaldehyde solution was completely converted to sugar by this agent at 100° in the course of 1 1/2 hours, with little formation of lead formate. Lead hydroxide precipitated with ammonia, as well as other bases investigated, did not show this powerful effect.

*For the experimental conditions and the analytical methods, see [4].

**Soda does not appear to have been tried previously as a condensing agent. Loew merely mentions generally that alkaline-reacting salts such as potassium sulfite and carbonate can affect condensation.

this salt maintains a small concentration of the free base for a long time; this concentration can be calculated from the easily determinable concentration of carbonate. Thus it is possible by the use of soda to follow changes in the concentration of base during the entire reaction.

Action of soda on formaldehyde. The curves in the following graph show the rates with which soda is consumed by formaldehyde under various conditions. It is seen that the first one-third of the soda content is consumed rapidly, while the soda content decreases only slowly as the reaction proceeds, until sugar formation occurs (in the uppermost curve). This is also true if the total soda content does not suffice to neutralize the formaldehyde. /42

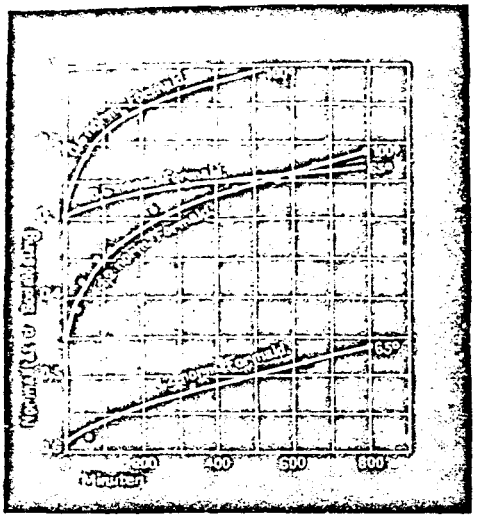

Figure. Abscissa: Minutes. Ordinate: Normality of Soda Solution. Curves (from top to bottom): 0.6 N Formaldehyde at 100°; 0.6 N Formaldehyde at 65°; 1.2 N Formaldehyde at 100°; 1.2 N Formaldehyde at 65°.

1.2 N Formaldehyde

Time	Normality of soda solution	
min.	65°	80°
0	0.085	0.086
50	0.069	0.054
100	0.062	0.047
200	0.055	0.041
400	0.048	0.033
800	0.044	—

Thus, for example, the content of the 0.085 N soda solution would suffice only for the conversion of 0.17 N formaldehyde into formate and methyl alcohol.

The following table shows when, and under what conditions, the formation of sugar is observed.

Formate formation before sugar formation begins

Initial concentrations of the solutions		Concentrations at start of sugar formation		Formaldehyde consumed before sugar formation in per cent
Formaldehyde normality	Soda normality	Formaldehyde normality	Soda normality	
2.1	3.2	0.50	2.4	76
1.2	0.6	0.40	0.20	67
0.6	0.3	0.26	0.13	57
0.45	1.1	0.19	0.97	58
0.45	0.22	0.27	0.13	40
0.30	0.90	0.18	0.84	40
0.30	0.72	0.18	0.66	40
0.30	0.12	0.20	0.07	33
0.15	0.36	0.09	0.33	40

The concentrations in the second columns are calculated on the assumption that the dissappearance of one equivalent of soda corresponds to the conversion of two equivalents of formaldehyde with the formation of formate.

The data collected in the latter table lead to the following conclusions:

1. The concentration of formaldehyde at the onset of sugar formation is directly dependent on the initial concentrations of formaldehyde and soda, in that sugar formation can always be observed only after the conversion of a definite amount of formaldehyde into formate and methyl alcohol. /43

2. The absolute concentration of formaldehyde at the point where sugar formation can first be observed, increases with the initial concentration; in concentrated solutions, the former increases much more slowly than the latter, but in greater dilutions (from 0.3 N downward), approximately in proportion.

3. The soda concentration most suitable for the condensation reaction is somewhat less than half of the aldehyde concentration. An increase in the amount of soda, leaving the formaldehyde concentration unchanged, favors the formation of formate to an especially large extent in concentrated solutions.

These results suggested the assumption that sugar condensation from formaldehyde is possible only when the formate concentration has attained a definite level. If this were the case, sugar must appear earlier, under otherwise identical conditions, in experiments in which formate is added from the beginning;

Effect of formate concentration of the solution on the formation of sugar

Initial concentration			Concentration at onset of sugar formation	
Formate normality	Formaldehyde normality	Soda normality	Formaldehyde normality	Soda normality
0	0.30	0.148	0.21	0.102
0.4	0.30	0.148	0.21	0.102
0.8	0.30	0.148	0.21	0.102

It is seen that addition of formate has no effect whatever on the onset of sugar formation.

The alkalinity of the soda solutions is sufficiently large to rapidly destroy the sugar which is formed, and to render it impossible to follow the formation of sugar quantitatively. This interference, which occurs with all bases, is avoided by using, in place of the latter, calcium carbonate. The reaction proceeds slowly, to be sure, but the sugar which is formed also is significantly longer lasting at elevated temperatures in the permanently neutral-reacting solution.

Using calcium carbonate as the condensation agent, the reaction takes the following course*: /44

Formaldehyde consumed, gram-moles per liter	0	0.20	0.56	0.63	0.67
Hours elapsed	0	10	13	14	Final value

Thus, in the first half of the reaction period the formaldehyde is consumed extraordinarily slowly, but the consumption of formaldehyde increases very rapidly in the second half of the reaction period.

It is therefore to be concluded that the condensation of formaldehyde to form sugar proceeds in several individual reaction steps. **

We were indeed able to show that in the formation of sugar by condensation of formaldehyde, glycolaldehyde is first formed.

This substance could be isolated in the form of its hydrazone and osazone (see next communication), if the condensation experiment is terminated soon after the start of sugar formation.

In addition, a condensation was followed quantitatively at the boiling point, in the following manner:

	Start	10 hours	13 hours	14 hours
Formaldehyde***	0.67	0.47	0.11	0
Formic acid + methyl alcohol	0	0.04	0.06	0.065
Easily reducing sugars (glycoaldehyde)	0	0.024	0.07	0.07
Total gram-moles formaldehyde	0.67	0.534	0.24	0.135
Difference: higher sugars (pentoses)	0	0.136	0.43	0.535

The results are all recalculated on the basis of the corresponding number of gram-moles/liter of formaldehyde. /45

*The reaction time using calcium carbonate is not appreciably affected by the addition of 0.2 gram-moles per liter of methyl alcohol; the methyl alcohol which is formed, therefore, does not act as a catalyst. Since the reaction curves indicate that a catalyst is formed during the course of the reaction, the effect of methylal was also investigated since the latter was next considered as a possible catalyst. Addition of 2 g methylal to 1 liter of formaldehyde, however, proved ineffective.

**E. Fischer has mentioned the possibility that glycolaldehyde and glyceraldehyde can occur in the assimilation of carbon in green plants [5].

***The formaldehyde was determined by the ammonia method, the formic acid (= methyl alcohol) from the amount of calcium dissolved, and the products denoted as nonreducing sugars by treatment with Fehlings solution (according to Brown and Morris) for 12 minutes at 45°.

It can be seen that the amounts of formaldehyde found in the three lower categories differ more and more from the original amount as the time continues. This can only be interpreted as showing that the easily reducing intermediate products (glycolose and any trioses) mediate in the formation of sugars (pentoses) which are nonreducing under the selected analytical conditions*.

To further clarify the reaction mechanism, it is necessary to determine more exactly the nature of the condensation products, and indeed to do this as far as possible with the exclusion of secondary reactions. Loew's condensation with lime was not well suited for this purpose. On the one hand, Lobry de Bruyn and Alberda van Ekenstein have shown that lime brings about rearrangements in the sugar group, and on the other hand the sugar which forms is rapidly destroyed by lime. Accordingly, then, Loew's formose presumably contains not merely the primary condensation products. Rather, it may be expected that the condensation with calcium carbonate, which proceeds in practically neutral solution, leads to the most homogeneous [i.e. uncontaminated] products possible.

8. On the Formation of i-Arabinoketose from Formaldehyde

H. Euler and A. Euler

As E. Fischer [6] has shown, the "formose" prepared by Loew via condensation of formaldehyde with lime is a mixture of at least three, and probably more, kinds of sugar. Of these, only oneproduct has been identified, namely α-acrose, identical with i-fructose. The presence of a pentose was deduced from Fischer's analyses of the osazones (loc. cit.). Loew [7] has also drawn conclusions regarding a pentose based on the furfurol reaction. Neuberg [8] was later able to show, with the aid of his methylphenylhydrazine reaction, that a ketopentose is a component of the formose obtained with lime, with the methylphenylosazone of the ketopentose melting at 137°. This compound differs considerably from the inactive methylphenylosazones of known constitution previously described, and according to Neuberg it must therefore possess a branched carbon chain, otherwise it cannot have the keto group in the α-position. /46

When we used calcium carbonate as the condensation agent, for reasons indicated in the preceding communication, we obtained other and better defined end products than Loew, and we wish to describe these below.

On boiling 1 liter of 2% formaldehyde solution with 10g calcium carbonate (freshly precipitated salt appears not to be appreciably more effective than previously dired salt) under reflux, the aldehyde is only very slightly attacked during the first 8-10 hours, but more rapidly in the subsequent hours, so that a full two-thirds of the total formaldehyde is consumed in the last one-third of the reaction period (cf. preceding communication), and goes predominantly into the formation of sugar.

Under these conditions appreciably less formate is produced than in alkaline solution. After the end of the reaction, only 5% of the formaldehyde had been converted to formate. In our condensation experiments with soda (cf. preceding communication), at least 17%, and in 0.67 N formaldehyde 30% of the aldehyde was consumed in formate production.

When all of the formaldehyde has disappeared, a syrup is obtained after condensation of the solution and precipitation of the calcium formate with alcohol and ether followed by distillation of the alcohol-ether solution. Osazones, in a yield of 50-80% of the formaldehyde used, are precipitated from this syrup by phenylhydrazine in acetic acid. This crude product is first thoroughly boiled with a rather large amount of water, removing a small portion which contains the most soluble osazones. The bulk of the material is now dried on clay sufficiently so that it can be treated with benzene. Now after the osazones are ground with a little cold benzene, which dissolves the dark colored and oily contaminants, the pressed product, in an amount representing about 30% of the formaldehyde used, is fairly pure and melts at 135-145°. It is fractionated by recrystallization, an operation which shows that it is almost homogeneous. After a small amount of an easily soluble osazone is extracted with benzene, the substance finally melts sharply at 166° (uncorr.) without prior sintering. The melting point does not increase on further recrystallization, and the compound thus proves to be completely pure. The analysis shows that a pentose is present here.

0.2392 g. substance: 0.5455 g. CO_2, 0.1320 g. H_2O. — 0.2653 g. substance: 39.33 cc. N (18.5°, 768 mm).

$C_{17}H_{20}N_4O_3$.	Calcd.	C 62.13,	H 6.15,	N 17.10
	Found	" 62.19	" 6.13	" 17.20.

The osazone has a pure yellow color like arsenic sulfide, dissolves very easily in alcohol, easily in hot 50% alcohol, with more difficulty in hot benzene, slightly in water and ether, and not at all in ligroin. Since it was likely that this compound is identical with i-arabinosazone, the melting point was determined on a cocrystallized mixture with i-arabinosazone, m.p. 160° (from l-arabinose, Kahlbaum). The mixed m.p. was found to be 159-161° (uncorr.). /47

The result allows hardly any other possibility than that the analyzed osazone is i-arabinosazone. The corresponding sugar may thus be arabinose or ribose. The latter assumption is excluded, since on reduction with sodium amalgam with continual neutralization of the solution (method of Kiliani [9] no adonite can be precipitated by treatment with benzaldehyde (E. Fischer [10]. Of the sugars corresponding to arabinosazine, arabinoaldose cannot be present in significant amounts, since no crystalline hydrazone could be obtained in the cold with p-bromophenylhydrazine even after several days. Instead, a solution separated, from which oily p-bromosazones deposited after two hours' heating on a water bath, and after a few days in the cold, a small amount of the characteristic

*Whether the distinct furfurol reaction of the condensation product is attributable to very small amounts of arabinose or to another sugar must remain undecided for the present. A test was made particularly for methylfurfurol by the method of Tollens and Widtsoe [11], but with negative result.

cold, a small amount of the characteristic i-arabinose-p-bromophenylhydrazone, m.p. 161°; it is also soluble with difficulty in hot water. It can be assumed that a small degree of conversion into arabinoaldose occurs on heating with phenylhydrazine.

The experiments reported lead to the assumption that the pentose which comprises the bulk of our condensation product is identical with i-arabinoketose.

In fact, Neuberg's resorcinol test for ketoses [12] is obtained very distinctly, and the bulk of the crude sugar readily undergoes reaction with methylphenylhydrazine.

Behavior toward methylphenylhydrazine: 7.5 g thick syrup, 15 g methylphenylhydrazine (Kahlbaum), 15 cc 50% acetic acid, and 15 g ethyl alcohol were mixed; the solution acquired a dark red color in the cold after a few minutes, in the manner characteristic for ketoses. Because of the ease with which resinification occurs, the solution was not heated. After 18 hours' standing, water precipitated a dark /48
oil, which, after extraction with ether, weighed 6 g. After several days, this oil deposited a small amount of crystalline osazone, which melted after purification at 137-138°, and is presumably identical with the osazone which Neuberg [13] obtained from Loew's formose. The crystalline product was insufficient for analysis, and the yield of crystalline osazone was not increased by purification with pyridine-ligroin. Therefore the oil itself was analyzed.

0.1733 g substance: 26.66 cc N (20.5°, 760 mm).
$C_{18}H_{23}N_4O_4$. Calcd. N 15.8. Found N 17.8.

The nitrogen content found, which is too high for arabinose methylphenylosazone, was not lowered by shaking the oil with 0.1 N sulfuric acid, and therefore may be attributed to the presence of lower osazones. We were therefore unsuccessful in preparing the methylphenylosazone of arabinoketose in pure form, but this in no way excludes the conclusion that it forms the principal component of the osazone oil.

Oxidation with bromine. 24 g of ca. 50% syrup was oxidized with 20 g bromine for 12 hours in the cold; the bromine went into solution in a few minutes. The hydrogen bromine was removed with silver carbonate and the filtrate boiled with calcium carbonate for 1/2 hour. After concentrating to a very small volume, a brown syrup remained, which was poured into alcohol, yielding a copious precipitate (5 g) of crystalline calcium salt.

After reprecipitation and drying over sulfuric acid, the salt was analyzed.

(1) 0.3034 g substance: weight loss at 100°: 0.0296 g; 0.1153 g $CaSO_4$.
(2) 0.218 g substance: weight loss at 100°: 0.021 g, weight loss at 150°: 0.020 g; 0.074 g $CaSO_4$.

$(C_4H_7O_5)_2Ca + 4\,H_2O$.

Calcd. $2\,H_2O$ 9.43, Ca 10.47

Found (1) H_2O (at 100°) 9.8 Ca 11.2
" (2) " " " 9.6, (at 150°) 9.2, Ca 10.0

It is seen that the values are in satisfactory agreement with the formula for calcium trihydroxybutyrate crystallized with 4 molecules of water. This result was confirmed by reduction of the salt with hydrogen iodide. The salt was boiled under reflux with hydrogen iodide, sp. gr. 1.7, and some red phosphorus for one day; a semi-solid oil soon deposited, which was easily dissolved in ether. The substance, after extraction with ether, was treated with zinc dust and sulfuric acid in the cold; steam distillation then gave a small amount of fatty acid. Neutralization of the acid with calcium carbonate afforded a small cluster of pointed leaflets of the crystalline calcium salt. /49

0.0777 g of desiccator-dried substance: weight loss at 100°: 0.0063 g: 0.0459 g $CaSO_4$.

$(C_4H_7O_2)_2Ca + H_2O$. Calcd. H_2O 7.8, Ca 17.2
Found " 8.1 " 17.4.

This compound, then, is calcium n-butyrate crystallized with one molecule of water. Corresponding with this, decomposition of the salt with sulfuric acid produced the penetrating odor of butyric acid.

In this way it was further confirmed that no significant amounts of aldopentoses are contained in the condensation product produced with calcium carbonate.

Oxidation with nitric acid: 10 g ca. 50% syrup, evaporated to dryness on a water bath with 12.5 g nitric acid, sp. gr. 1.2, after vigorous oxidation, gave on boiling with calcium carbonate, concentration of the filtrate, and precipitation with alcohol, a copious quantity of the above-described calcium trihydroxybutrate.

0.2707 g substance (dried over sulfuric acid): weight loss at 100°: 0.0265 g; 0.0922 g $CaSO_4$.

$(C_4H_7O_5)_2Ca + 4H_2O$. Calcd. $2H_2O$ 9.43, Ca 10.47.
Found " 9.80 " 10.00.

The oxidation also produced oxalic acid as a by-product. On the other hand, even on repeated, still longer digestion with nitric acid on the water bath, no trihydroxyglutaric acid could be obtained: a product which would necessarily be formed from aldoarabinose and is readily detectable as the difficulty soluble calcium salt.

It was mentioned above that along with the major quantity of osazone (arabinosazone, m.p. 166°), a small amount of a more easily soluble osazone, m.p. 140-142° (uncorr.) was isolated. The analysis agrees with the values calculated for a hexosazone.

0.1155 g substance: 15.6 cc N (18°, 762 mm).
$C_{18}H_{22}N_4O_4$. Calcd. N 15.64. Found N 15.8.

The amount of substance available was insufficient for further investigation. It is easily soluble in ether, and extremely easily soluble in benzene, from which it is precipitated by petroleum ether.

If the condensation experiment with calcium carbonate is terminated shortly /50
before one-half of the formaldehyde has reacted, the solution that contains less of reducing substances, which however, react with Fehling's solution to a large extent even in the cold. The syrup obtained by evaporation, because of its formaldehyde or trioxymethylene content, likewise gives an oily precipitate with phenylhydrazine in the cold. Even after removal of the latter, * methylenephenylhydrazine crystallizes over a long period of time from the osazone oil which is obtained from the filtered solution on warming with phenylhydrazine. In order to avoid the interfering effect of formaldehyde, we attempted to remove the latter completely by precipitation with p-dihydraziondiphenyl [14]. After concentration of the filtrate to a small volume and filtration to remove any small amounts of the dihydrazine, an easily resinifying oil was prepared in the usual way with phenylhydrazine. Extraction of this oil with boiling pyridineligroin resulted in small amounts of a finally crystalline osazone, which melted, not sharply, at 180° (uncorr). not sharply, at 180° (uncorr).

0.860 g substance: 17.8 cc N (16°, 750 mm).
$C_{14}H_{14}N_4$. Calcd. N 23.6. Found N 24.0.

Thus the nitrogen content corresponds to the composition of glycolosazone, whose presence was further confirmed by the preparation of the corresponding, hitherto unknown phenylhydrazone.

After a few weeks, indeed, colorless scales crystallized from a fraction of the osazone oil difficulty soluble in pyridine-ligroin. They are very easily soluble in common solvents (water, alcohol, ether), and melt at about 162°.

0.0585 g substance: 9.85 cc N (17°, 735 mm).
$C_8H_{10}N_2O$. Calcd. N 18.7. Found N 19.3.

The presence of glycolaldehyde is thus established. Dihydroxyacetone was /51
also isolated in the form of its methylphenylosazone, m.p. 127°. In contrast, the search for glyceraldehyde using the phloroglucinol test (of Wohl and Neuberg [15] has thus far been in vain.

*It may be mentioned here that this methylenephenylhydrazine melted at a constant 168.5° after boiling twice with benzene.

0.2068 g substance: 41.0 cc N (17.8°, 760 mm).
$C_7H_8N_2$. Calcd. N 23.26. Found N 23.27.

It crystallizes repeatedly from the benzene solution in scales, m.p. 128°, which probably have the simple (unit) molecular size. Based on the boiling point determination Walker [16], varying melting points of 146-155° are associated with the simple molecular weight. However, Walker once found 128°.

REFERENCES

1. Euler, H. and Euler, A.: Berichte der Deutschen Chemischen Gesellschaft, Vol. 38, p. 2551, 1905.
2. Auerbach, ibid., No. 12, p. 2733.
3. Fresenius, W. and Grünhut, L.: Z. anal. Chem., Vol. 44, p. 13, 1905.
4. Svenska Vet. Akad. Arkiv. f. Kemi, Vol. 2, No. 10, 1905.
5. Fischer, E.: Berichte der Deutschen Chemischen Gesellschaft, Vol. 23, p. 2238, 1890.
6. Ibid., Vol. 21, p. 988, 1888; Vol. 22, p. 359, 1889.
7. Loew, O.: Chem. Ztg., Vol. 21, p. 243, 1897.
8. Neuberg: Berichte der Deutschen Chemischen Gesellschaft, Vol. 35, p. 2632, 1902.
9. Kiliani, ibid., Vol. 20, p. 1233, 1887.
10. Fischer, E.: ibid., Vol. 26, p. 638, 1893.
11. Tollens and Widtsoe: ibid., Vol. 33, p. 132, 1900.
12. Neuberg: Z. physiol. Chem., Vol. 31, p. 364.
13. Neuberg: Berichte der Deutschen Chemischen Gesellschaft, Vol. 35, p. 2632, 1902.
14. Ibid., Vol. 32, p. 1961, 1899.
15. Wohl and Neuberg: ibid., Vol. 33, p. 3104, 1900.
16. Walker: J. Chem. Socl. Vol. 69, p. 1283.

Translated for the National Aeronautics and Space Administration by Scripta Technica, Inc., NASw-1694.